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# Thermal Expansion and Swelling of Cured Epoxy Resin Used in Graphite/Epoxy Composite Materials

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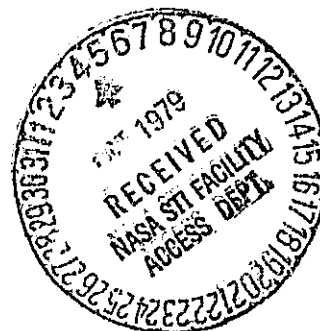
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# **Thermal Expansion and Swelling of Cured Epoxy Resin Used in Graphite/Epoxy Composite Materials**

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National Aeronautics and  
Space Administration

Thermal expansion and swelling of cured epoxy resin  
used in graphite/epoxy composite materials

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ABSTRACT

Thermal expansion and moisture absorption of graphite/epoxy composites can affect the other physical properties of these materials. Since the fibers are not significantly influenced by either parameter, these effects come about through influences on the resin matrix. Therefore, this study is focused on cured resin behavior. It was found that the polymer swells by an amount slightly less than the volume of the absorbed water and that the swelling efficiency of the water varies with the moisture content of the polymer. Additionally, the thermal expansion of cured epoxy resin that is saturated with water is observed to be more than twice that of dry resin. Results also indicate that cured resin that contains near-equilibrium concentrations of water at 95° C will absorb up to 21% additional water when placed in 1° C water. The mechanism for this phenomenon, termed reverse-thermal-effect, has not been reported before; it is described in terms of a slightly modified free-volume theory in conjunction with the theory of polar molecule interaction. Nearly identical behavior was observed in two graphite/epoxy composite systems, thus establishing that this behavior is common to all cured epoxy resins.

## 1. Introduction

Real-life service environments experienced by graphite/epoxy composites can be complex and variable. Thermal expansion and swelling are two specific responses of a composite material to temperature and moisture variations in the service environment. These two particular response parameters are very important in composites because they can significantly influence the mechanical behavior of composites through the buildup of residual stresses between the fibers and the matrix. It is known that graphite fibers are not significantly affected by the presence of moisture or by the temperature changes experienced in real-life conditions and thus, thermal expansion and swelling must come about through the influences of temperature and moisture on resin matrix material [1-4].

The initial behavior of the complex moisture absorption process in a resin below its glass transition temperature ( $T_g$ ) can be mathematically described by the laws of classical diffusion [5]. The glass transition temperature ( $T_g$ ) is defined as that temperature below which the resin is in the "glassy" rather than the "rubbery" state. The relationship between resin swelling and  $T_g$  during isothermal absorption is fairly well understood [6]. Temperature variations during absorption, however, can permanently and significantly alter sorption behavior [7]. Accepted theoretical concepts for polymeric materials [8-11] have not been used to describe changes in swelling and thermal expansion behavior resulting from temperature variation during absorption.

The present paper presents experimental findings regarding thermal expansion and swelling of resin material as influenced by variations in temperature during moisture absorption for temperatures below  $T_g$ . All data were obtained by water immersion with the exception of one test performed in 100% relative humidity to demonstrate similarity of response between vapor and liquid immersion. The temperature range investigated was from  $1^{\circ}\text{C}$  to  $95^{\circ}\text{C}$ , thus avoiding possible complications caused by the formation of ice or steam. To demonstrate that the information in this study is, in principle, applicable to resin/fiber systems, a limited number of comparison measurements using composites constructed of graphite fibers and each of two epoxy resin matrices were included. Finally, polymer theory relative to these findings is discussed and modifications to currently accepted concepts are proposed.

## 2. Experimental

### 2.1. Materials

The resin material used in this study was Hercules 3501-5 resin (Hercules Incorporated, Magna, Utah). The resin casting was prepared by Lockheed Missiles and Space Corporation (Sunnyvale, California) using glass plates separated by spacers that were about 0.125 in. (3.2 mm) thick. The uncured resin was heated to  $93^{\circ}\text{C}$  ( $200^{\circ}\text{F}$ ) under vacuum until all of the air was removed (about 1.53 h). It was then poured into the glass mold which was preheated to  $93^{\circ}\text{C}$ . The vertical assembly was placed in a vacuum oven at  $93^{\circ}\text{C}$  for 1 h, the temperature was increased to  $121^{\circ}\text{C}$  ( $250^{\circ}\text{F}$ ) and held for 1 h, and then increased to  $177^{\circ}\text{C}$  ( $350^{\circ}\text{F}$ ) and held for 45 min.

The composite materials of this study were also prepared by Lockheed, using Hercules AS/1501 prepreg tape and Fiberite Corporation T300/934 prepreg tape. Both composites were fabricated, using the standard 177° C (350° F) cure procedure, as sheets approximately 0.1 in. (2.5 mm) thick. The details of the composite fabrication technique are described elsewhere [12].

## 2.2. Procedure

Rectangular specimens 0.5 in. (12.5 mm) wide by 4 in. (100 mm) were cut from the resin and composite sheets. Composite specimens were oriented so that the fibers were parallel to the long axis of the specimens. Peel-plyes were removed and all specimens were degreased with methyl alcohol and air-dried at room temperature. Residual moisture was removed from the specimens by further drying in a heated vacuum dessicator at either 100° C or 40° C until the rate of weight loss became less than  $5 \times 10^{-5}$  g/day - a process that usually required at least 30 days.

The specimens were moisture conditioned by immersion in distilled water, with the desired water temperature controlled to better than  $\pm 0.5^\circ$  C, using a constant temperature bath. One resin specimen was subjected to 100% relative humidity at room temperature for 50 days after first having been conditioned in water. Some resin specimens, after conditioning in water, were removed and placed inside plastic bags to minimize moisture exchange while they were being thermally equilibrated during measurement of "wet" thermal expansion behavior. Low-temperature exposure was accomplished by use of a refrigerator with

specimens either immersed in water or placed in plastic bags as required. Thermal expansion determinations on dry specimens were performed in an oven capable of controlling temperature to within  $\pm 1^\circ \text{C}$ . Specimens were allowed at least 1 h to equilibrate at each temperature. Longer equilibration times of up to 24 h produced no change in volume compared with that measured after 1 h for the dry specimens.

Specimen volume was calculated from length, thickness, and width measurements made with micrometers accurate to  $\pm 0.002 \text{ in}$ . For each specimen, thickness and width were calculated as the average of three measurements, one at the center and one near each end. Length was determined from the average of measurements made at each of two edges. To minimize error caused by thermal expansion, great care was taken to ensure that each specimen was removed from its environment for no more than 15 sec during each dimensional measurement. Following the volumetric determination, weight change measurements were performed. Specimens were wiped using a lint-free towel and air dried at room temperature for 5 min. This procedure eliminated possible error caused by specimen heat upsetting the balance zero and by uncertainty of surface water quantity. Specimen weight was determined using a Mettler analytical balance which was accurate to  $\pm 0.05 \text{ mg}$ . Weight loss differences for saturated specimens were negligible regardless of initial temperature for the 5-min weighing interval.

### 3. Background

As a basis for understanding the experimental results, it is necessary to define terms and discuss certain theoretical concepts.



The terms "cured epoxy resin" and "resin" refer to a highly cross-linked polymeric material that can be considered to be an "infinite network" [8]. Because the network structure inhibits molecular (segmental) mobility [8, 9, 11], cross-linked polymers can exist in a "rubbery" or "leathery" state above  $T_g$  [9, 13, 14]. When used as a matrix material in composites, the resin must be rigid, or in the "glassy" state, that is below  $T_g$ , to effectively transfer energy to the fibers [2, 15-18].

"Thermal expansion" is used here to describe volumetric changes caused solely by variations in temperature at constant moisture content. "Swelling" is used to describe volumetric changes due to moisture content alone, independent of thermal expansion.

We can better understand thermal expansion and swelling as well as the phenomenon of the glass transition through a consideration of the resin's "occupied volume" and "free volume." Occupied volume is defined as that volume occupied by the actual mass of a molecule plus the volume it occupies because of thermally dependent harmonic vibration that excludes all other molecules from its domain. For example, at absolute zero, the volume occupied by a polymer, if all its molecules were perfectly packed in contact with neighboring molecules, would be equal to the mass volume of the molecules. As temperature is increased above absolute zero, however, molecular vibrations increase and all the molecules begin to occupy more volume. Thus, occupied volume is dependent on temperature because thermally induced molecular motion causes each molecule (or molecular segment in the case of a cross-linked polymer) to move about its equilibrium position, therefore occupying more space than

its actual mass volume [9]. If the molecules were to remain packed so that their domains were in perfect contact, the occupied volume of the polymer at any temperature would exactly equal the sum of the actual mass volume of the molecules and their vibrational volume. The molecules are not perfectly packed, however, and free volume is defined here as the difference between the measured volume of a polymer and the occupied volume. This difference is the result of "holes" or "voids" caused by packing irregularities [8, 10].

For a molecule or molecular segment to change position, it must:

- (1) have access to enough free volume to accommodate its occupied volume, and
- (2) possess enough energy to permit the position change [8-11].

The glass transition temperature,  $T_g$ , can be described as the temperature above which molecules (or molecular segments) possess adequate energy and have access to adequate free volume for molecular rearrangement to occur. Below  $T_g$  their motion is restricted to such a degree that the polymer appears hard and glassy or "frozen" [11]. As a polymer is cooled through  $T_g$ , an abrupt decrease in coefficient of expansion is encountered. This is because the free volume continually decreases as  $T_g$  is approached from above until a critical value is reached which is too small to allow molecules (or molecular segments) to change position [9, 19]. This critical free-volume fraction at  $T_g$  for most polymers and many other substances is about  $1/40$  ( $2.5 \pm 0.3\%$ ) of the total volume occupied by the substance [8-10]. According to the concepts presented by both Bueche [9] and Ferry [10], the only volume contraction below  $T_g$  is of a solid-like character. Bueche assumed the amount of free volume remaining is a variable function of temperature, and Ferry assumed that the

amount remains constant. It is also essential to note that the total volume of a polymer (occupied volume plus free volume) at a temperature below  $T_g$  is greater the more rapidly the polymer is cooled to that temperature [11]. This implies that if the cooling rate is greater than the rate of molecular rearrangement, free volume can increase. Thus, although a molecule may have enough available free volume to change position, it cannot do so when there is inadequate available energy.

Cured epoxy resin contains polar hydroxyl groups which, because they retain a certain degree of steric freedom, are able to hydrogen bond by alignment with similar groups located on nearby segments. Rehage and Borchard [11] have reported that these bonds become more numerous as temperature decreases. These temperature-dependent bonds have an effect on the polymer expansion coefficient. The water molecule is also polar, and thus will be attracted to the polar hydroxyl groups found in the resin. Once at the polar site, the water molecule is capable of hydrogen bonding to the hydroxyl group, thereby disrupting the interchain hydrogen bonding with the net effect of changing the interchain bond length and increasing the freedom of segment motion [13, 20]. The resulting volume change in the polymer is similar to that caused by an increase in temperature. Thermodynamic arguments have shown that liquid molecules can combine with polymer molecules in the glassy state and actually become part of the glassy structure, establishing an equilibrium between the liquid and glassy mixed phase. In a cross-linked system, a glass, when compared to a melt, retains a structure that requires more space and can, therefore, absorb more liquid [11].

The result of water combining with a polymer in the glass state is an increase in the occupied volume of the polymer equal to the occupied volume of the attached water. It has been observed, however, that the resulting volume of the polymer/water structure is slightly less than the sum of the independent volumes of absorbed water and of dry polymer [8, 14]. Various works [21-24] suggest that water molecules can exist in polymeric media in two states: bound to the polymer molecule and unbound. It is assumed that bound water molecules are immobilized and that unbound molecules are contained in the polymer's free volume and are relatively free to travel through the free-volume voids.

Finally, to better understand the shapes of absorption and swelling curves, it is necessary to note that the network structure of cross-linked epoxy resins is not homogeneous (as generally assumed), but is really a mixture of highly cross-linked micro-gel particles (or micelles) embedded in a less highly cross-linked matrix. Because of their higher density, the micelles are less easily penetrated by water than is the surrounding matrix. Although they are comparatively more dense, the micelles do contain a portion of the total polymer free volume. This two-phase network structure has been observed by optical microscopic techniques [14, 25-30].

In summary, a cured epoxy resin below  $T_g$  is a rigid network structure, highly resistant to molecular rearrangement so that free-volume collapse is unlikely. Free-volume magnitude, however, is (in theory) inversely influenced by molecular vibrational volume because as temperature below  $T_g$  is reduced, the molecular segments vibrate less;

therefore, they occupy less of the intermolecular space (free volume). Water molecules may either occupy free volume causing no swelling or interrupt interchain hydrogen bonding causing swelling.

#### 4. Results and discussion

##### 4.1. Isothermal absorption process

The mathematical theory of moisture absorption in a resin has been described elsewhere [5, 31] and will not be discussed here. In view of the information presented in the background section of this report, however, the shape of the isothermal absorption curve indicates the physical processes involved in absorption. Fig. 1 is a typical plot of percent weight gain vs square root of time for 3501 resin immersed in 74° C water. Note that initially the absorption curve is linear with the square root of time to slightly less than 4% weight gain. This linearity suggests that absorption is predominantly diffusion-controlled in this region [5, 31]. Above 4% moisture, the specimen begins to fill with moisture and the absorption rate begins to decrease. Finally, equilibrium moisture content is approached, although rate of approach is extremely slow. Even after 144 days, the specimen is still gaining weight (Fig. 1). Actual equilibrium may not be achieved for perhaps years in this resin. These observations suggest that the final absorption process is difficult, perhaps reflecting the difficulty with which water enters the highly cross-linked micro-gel particles or micelles within the resin.

#### 4.2. Swelling

Fig. 2 describes the swelling of 3501 resin as moisture is absorbed at 74° C. All dimensions were determined while the specimen was at 74° C. This figure shows the percent change in resin volume (compared with the volume of dry resin,  $V_0$ ) as a function of the volume of absorbed water calculated from the change in specimen weight (normalized to the volume of the dry resin,  $V_0$ ). Additionally, a dashed line having a slope of 1 is shown in Fig. 2; it represents swelling that would be expected if the volumes of the dry resin and the absorbed water were additive. As can be seen from Fig. 2, the swelling of the 3501 resin as a function of absorbed moisture is rather complex; however, it can be roughly divided into three regions: Region I, from essentially zero moisture to from 3% to 4% moisture, in which swelling of the resin is far less than the volume of water absorbed; Region II, from 3% to 4% moisture up to 6% moisture, in which swelling of the resin about equals the volume of absorbed water; and Region III, above 6% moisture, where again swelling is less than the volume of water absorbed.

Region I corresponds roughly to the region of diffusion-controlled absorption observed in Fig. 1. This suggests that as water is initially absorbed and diffuses into the resin, some of the water begins to occupy polymer free volume, causing no swelling, while some of the water disrupts interchain hydrogen bonds, causing swelling by hydrogen bonding with the resin. As diffusion gives way to equilibration at between 3 and 4 weight percent moisture, the process of interchain hydrogen-bond disruption dominates. As individual water molecules are "removed" from the free volume by combining with the resin, they are replaced by

diffusion of moisture from outside the specimen; hence, there is the nearly one-to-one correspondence between swelling and volume of moisture absorbed in swelling Region II. Above about 6% moisture concentration, the apparent swelling efficiency drops far below that experienced in the first two swelling regions. This low efficiency reflects diffusion into the high-density micelles, which contain some free volume but due to their highly reacted state (dominated by covalent bonding) swell only slightly.

The last data point on Fig. 2, representing the volume increase of the resin/water system as a function of volume of water absorbed, is very close to the equilibrium volume, although time to reach equilibrium may still be very long. At this point, the difference between the actual volume increase and the expected value for additive volumes, the dashed line with a slope of 1 (Fig. 2), presents the amount by which the wet polymer volume differs from the sum of its original dry volume and the volume of absorbed water. If it is assumed that water occupying the polymer free volume does not cause polymer swelling, the 2.64% value derived from Fig. 2 is in reasonable agreement with the assumption that the free-volume quantity for polymers below  $T_g$  is about 1/40 (2.5%) of the total volume [10].

Finally, it is realized that a density increase in the resin caused by additional cure during the course of the absorption tests would result in an apparent reduced swelling efficiency; however, the measured dry densities of the resin before (1.2591 g/cm<sup>3</sup>) and after (1.2581 g/cm<sup>3</sup>) absorption indicate no additional cure occurred during the test period.

#### 4.3. Variable-temperature absorption process (reverse-thermal-effect)

Perhaps the most interesting moisture absorption phenomenon is illustrated in Fig. 3, in which the percent weight gain vs exposure time for two identical 3501 resin specimens, initially immersed in 74° C water, is plotted. When both specimens had achieved a moisture concentration of about 3.8% (about the same point at which a plot of percent weight gain vs square root of time becomes nonlinear (Fig. 1), and about the same concentration where swelling efficiency begins to increase (Fig. 2)), one specimen was removed and immersed in 25° C water. This reduced temperature resulted in a reduced absorption rate as shown by the lower dashed curve in Fig. 3. This behavior was expected since absorption theory predicts that the absorption rate would be reduced by a lower temperature [5]. The other specimen was allowed to remain in 74° C water for 144 days (well into the micelle-filling Region III, Fig. 2). This specimen was then placed in 25° C water. Instead of a reduced rate of absorption as expected from theory [5] and demonstrated by the first specimen, the result was an increase in rate of absorption with the reduced temperature as shown in the upper dashed curve in Fig. 3. Although the specimen appeared to be nearing equilibrium, it showed a definite increased capacity for water at the lower temperature. This behavior was observed for 50 days until the specimen began approaching what appeared to be a new equilibrium. When the specimen was returned to 74° C water, rapid desorption occurred. Within 3 days, the moisture concentration returned to a value very near to that extrapolated from the original 74° C absorption curve and shown in Fig. 3. For brevity, this effect will be referred to as "reverse-thermal-effect." The



observation of this effect was surprising, for it has not been reported in previous studies; however, reverse-thermal-effect had been predicted and thermodynamically justified by Rehage and Borchard [11]. Their explanation is based on the reasoning that a solvent combines with the glassy polymer in the "frozen" state, that the freeze-in heat of the solvent is liberated, and that, as a result, the cross-linked mixed phase retains a structure requiring more space and can, therefore, absorb more solvent.

To illustrate the temperature dependence of the reverse-thermal-effect, equilibrium moisture concentrations at various temperatures were obtained using a single resin specimen that had been first allowed to approach equilibrium (except for micelle filling) in 74° C water. The result is illustrated in Fig. 4, which is a plot of weight-percent water at what appears to be equilibrium as a function of temperature; note the inverse linear relationship. Concurrent volumetric determinations at the various temperatures reveal that equilibrium volume of the resin is constant. Thus, the implication is that thermal expansion (or contraction) is compensated by swelling. To determine the mechanism that allows a specimen to contain 8.5% moisture at 1° C and 7.3% moisture at 74° C while retaining the same equilibrium volume, additional data regarding the magnitude of free volume and the magnitude of thermal expansion of wet (saturated) resin were generated. The free volume present in 3501 resin at 40° C was determined from the swelling curve shown in Fig. 5. That figure is similar to Fig. 2, in that the swelling efficiency is again illustrated in terms of percent-volume increase as a function of volume of moisture absorbed, normalized by the dry resin volume ( $V_0$ ).

Comparing Figs. 2 and 5, two significant differences can be noted. First, the change in slope, signifying increased swelling efficiency (transition from Region I to II), occurs after a greater volume of water is absorbed for the 40° C specimen than for the 74° C specimen. That difference suggests that more easily accessible free volume (as opposed to that contained inside micelles) is available at the lower temperature. Second, free volume calculated from the data obtained at 40° C (3.02% in Fig. 5) is larger than that found at 74° C (2.64% in Fig. 2). These data together imply that free volume increases as temperature decreases below  $T_g$ .

#### 4.4. High relative humidity and reverse-thermal-effect

To determine whether reverse-thermal-effect is unique to specimens immersed in water, a resin specimen was immersed in 74° C water to equilibrium and then exposed to 100% relative humidity at 25° C. Reverse-thermal-effect behavior was identical to that of immersed specimens. Immersion is not a required condition for reverse-thermal-effect.

#### 4.5. Composites and reverse-thermal-effect

The reverse-thermal-effect is not a property unique to 3501 resin material; it can occur in graphite/epoxy composite material and in other resin systems. Four composite specimens each of two composite systems were immersed in 74° C water to equilibrium and then placed in 25° C water to equilibrium. The two systems investigated were AS fibers in Hercules 3501 resin and Union Carbide T300 fibers in Fiberite 934 resin

(both having about 60% by volume fiber). The saturation weight-percent values at each temperature for each system are compared in Table I.

Table I Reverse-thermal-effect — two composite systems compared.

Immersion to equilibrium at 74° C followed by immersion to equilibrium at 25° C.

Specimen type	Wt %, 74° C	Wt %, 25° C
AS/3501	1.717 ± 0.013	2.002 ± 0.020
T300/934	1.803 ± 0.067	2.128 ± 0.080

As can be seen from Table I, the reverse-thermal-effect is essentially the same for the two different composite systems. It must, therefore, be included as one of the important physical properties to be considered when resin systems are being evaluated for applicability.

#### 4.6. Thermal expansion

Because moisture interacts with the resin hydroxyl groups, which influence thermal expansion behavior, the determination of thermal expansion values is not a simple matter. For clarity, we will first consider thermal expansion in the dry resin followed by that in the wet resin.

The effect of change in temperature on dry 3501 resin is shown in Fig. 6, which is a plot of volume, normalized by dividing each increase in resin specimen volume by its volume at 0° C, as a function of temperature. The data of Fig. 6 give a volumetric thermal expansion coefficient

of  $8.0 \pm 0.5 \times 10^{-5}/^{\circ}\text{C}^{-1}$ . Since it is known that past environmental exposures influence polymeric behavior [6, 32] it is felt that thermal expansion coefficient values, although not absolute, can be used as estimates. To illustrate, Fig. 7 presents a similar plot for a resin specimen exposed to moisture saturation and to several temperature variations prior to being dried. In this case, the coefficient has increased to  $9.4 \pm 0.5 \times 10^{-5}/^{\circ}\text{C}^{-1}$ .

Thermal expansion behavior of the wet 3501 resin originally saturated at  $74^{\circ}\text{C}$  is shown in Fig. 8. Care was taken to ensure that the weight-percent water (equilibrium moisture content at  $74^{\circ}\text{C}$ ) remained constant throughout the entire test series. Data were obtained first at  $74^{\circ}\text{C}$ , then at  $24^{\circ}\text{C}$ ,  $1^{\circ}\text{C}$ , and  $60^{\circ}\text{C}$ , allowing 1 h at each temperature to establish thermodynamic equilibrium. The volume decreased linearly with temperature at the three higher temperatures; however, the volume change at  $1^{\circ}\text{C}$  was much less than would have been anticipated. Because 1 h may not have been sufficient time to establish thermodynamic equilibrium at  $1^{\circ}\text{C}$ , exposure was increased to 24 h. The increased exposure brought the data in line with those expected from an extrapolation of the data from the higher temperatures. The difficulty in achieving thermodynamic equilibrium at  $1^{\circ}\text{C}$  was verified by raising the specimen temperature to  $24^{\circ}\text{C}$  for 1 h and repeating the measurements at  $24^{\circ}\text{C}$  and  $1^{\circ}\text{C}$  with identical results. Those data are shown in Fig. 8, which is a plot of change in specimen volume normalized to the wet specimen volume at  $0^{\circ}\text{C}$ , as a function of temperature. As can be seen, the wet thermal expansion coefficient, when given enough time for thermodynamic equilibrium, is  $1.9 \pm 0.05 \times 10^{-4}/^{\circ}\text{C}$  over the temperature range of  $74^{\circ}\text{C}$  to  $1^{\circ}\text{C}$ .

The increased magnitude of the wet thermal expansion coefficient compared with the dry, and the increased difficulty in attaining thermodynamic equilibrium in the wet condition, can be explained by the concept of free volume having an inverse relationship to temperature. If thermodynamic equilibrium between bound (frozen-in) water and unbound water is assumed for a resin specimen at equilibrium in 74° C water, and if it is assumed that unbound water occupies the available free volume, then it is reasonable to expect a shift in equilibrium between bound and unbound water toward the latter if additional free volume is made available by a reduction in temperature. If these assumptions are valid, then, in addition to the normal thermal contraction caused by a temperature decrease, further contraction must occur if bound water molecules become unbound, thus satisfying new equilibrium conditions created by additional available free volume. Thus, although it was previously established that 1 h is adequate for dry resin to adjust to temperature change (Fig. 6), it appears that wet resin requires more adjustment time because the equilibration time between bound and unbound water is apparently longer than 1 h when the temperature is reduced from 24° C to 1° C (Fig. 8). This result seems reasonable since at lower temperatures there is less available energy to convert solvent molecules from the "frozen-in" (bound) state to the liquid (unbound) state. Similar arguments can be applied to explain the fact that 1 h is adequate for wet resin to achieve equilibrium when its temperature is increased to 24° C from 1° C. Accompanying increased temperature is a decrease in available free volume, resulting in a shift in the equilibrium between bound and unbound water toward bound water. Because freeze-in heat is liberated

In this case, there is ample time and energy for thermodynamic equilibration. Thermal expansion and increased bond disruption caused by additional bound water both contribute to the wet thermal expansion coefficient of  $1.9 \pm 0.5 \times 10^{-4}/^{\circ}\text{C}$ .

#### 4.7. Swelling and free-volume changes during the reverse-thermal-effect

To fully understand the interrelationship of the mechanisms of swelling and free-volume change as functions of temperature, we will consider results of volumetric determinations obtained as a single resin specimen is first equilibrated in  $74^{\circ}\text{C}$  water and then equilibrated in  $1^{\circ}\text{C}$  water. The equilibrium volumes are identical. Again, thermal expansion and swelling compensate each other. This implies that although new hydrogen bonds are formed when the temperature is reduced to  $1^{\circ}\text{C}$ , they are disrupted by the absorption of additional water according to the rules of reverse-thermal-effect. Another observation is that the equilibrium-volume-percent water contained in the resin increased to 9.519 at  $1^{\circ}\text{C}$ . The measured resin volume increase over the dry resin volume at  $1^{\circ}\text{C}$  amounted to a volume percent of 6.099. Subtracting the actual resin volume percent increase from the volume percent water contained in the resin (the same procedure as used in Figs. 2 and 7) yields a free volume of 3.42% at  $1^{\circ}\text{C}$ . A plot of the three experimentally determined values for free volume (3.42% at  $1^{\circ}\text{C}$ , 3.02% at  $40^{\circ}\text{C}$ , and 2.64% at  $74^{\circ}\text{C}$ ) is shown in Fig. 9. As can be seen, the data fit a straight line with negative slope. Apparently free-volume-magnitude dependence on temperature can be readily determined by swelling curves, using as few as two exposure temperatures.

## 5. Conclusions

The swelling efficiency of water absorbed below the glass transition temperature by Hercules 3501 cured epoxy resin is temperature-dependent and concentration-dependent. The volume of unbound absorbed water that does not contribute to swelling is very near the accepted theoretical value for the free volume of a glassy polymer. The data are interpreted by a new theoretical model based on an equilibrium between bound water (which produces swelling) and unbound water and on an inverse relationship of free volume to temperature.

A phenomenon called reverse-thermal-effect, which involves greater water absorption at lower temperatures, occurs in the range of 1° C to 74° C when a specimen equilibrated in a wet environment at an elevated temperature is placed in a wet environment at a lower temperature. This effect, not reported elsewhere, can also be explained by use of the same proposed theoretical model in which the free volume in a glassy cross-linked polymer increases as temperature is decreased. Reverse-thermal-effect is similar in two composite systems and should be considered when the properties of any composite containing epoxy are being evaluated.

The coefficient of thermal expansion of water-saturated Hercules 3501 cured epoxy resin is greater than that of the dry resin in the range of 1° C to 74° C. It has also been shown that thermal expansion is compensated by swelling. These phenomena conform to the theoretical model.

Although this work establishes the concepts required for understanding the mechanism of moisture sorption in cured epoxy resin, further work extending the temperature range and establishing temperature and concentration threshold values is recommended.

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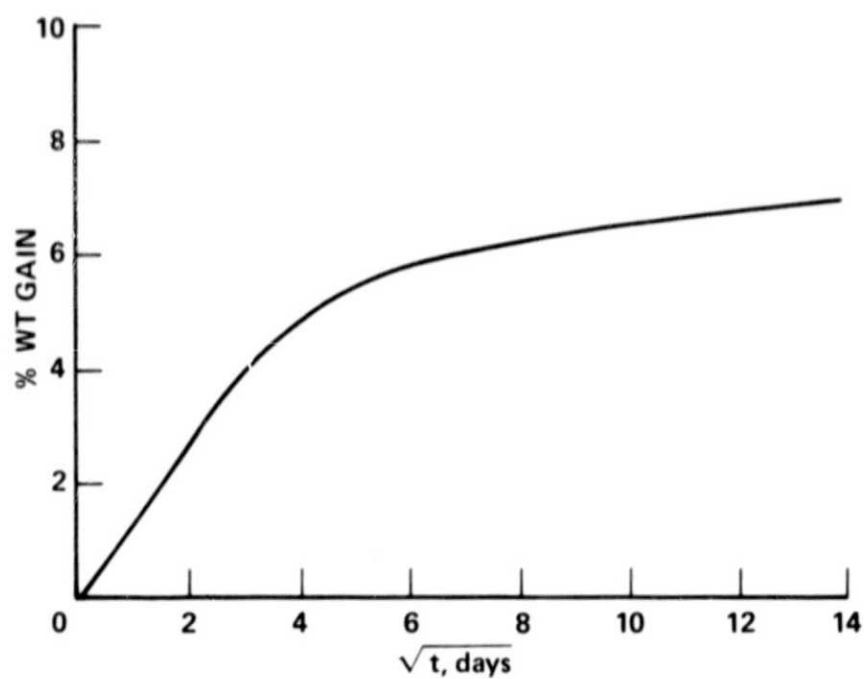


Figure 1.- Absorption curve, Hercules 3501 resin specimen fully immersed in 74° C water.

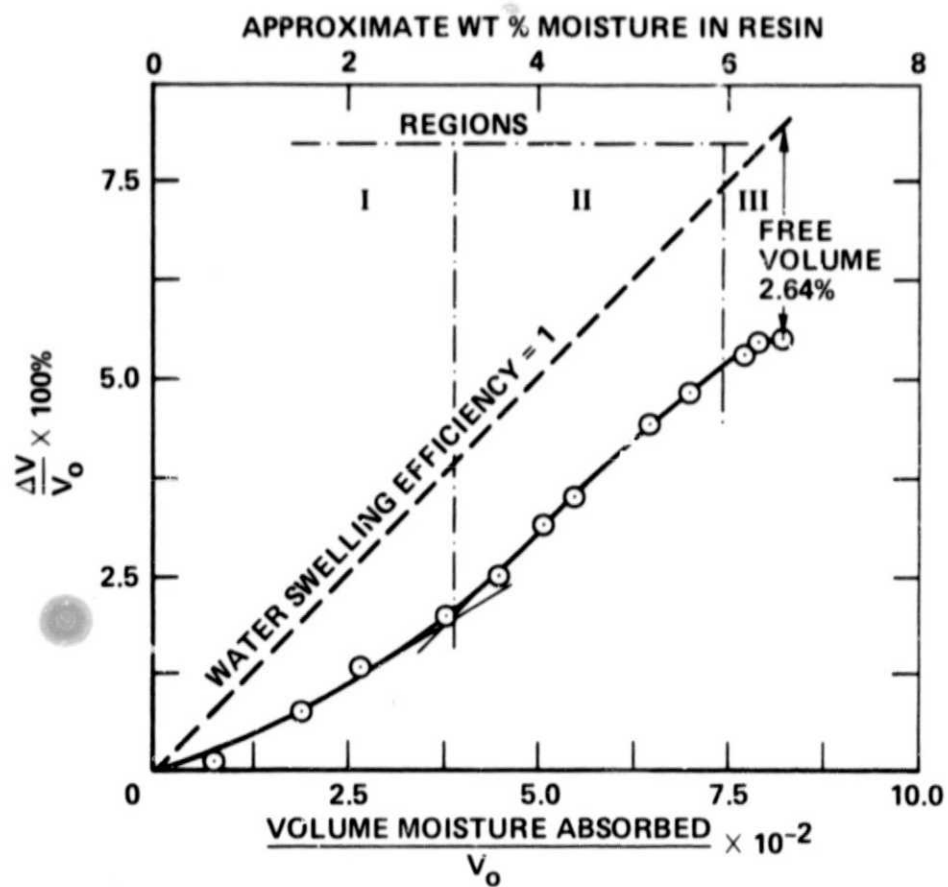


Figure 2.- Swelling efficiency of Hercules 3501 resin immersed in 74° C water.

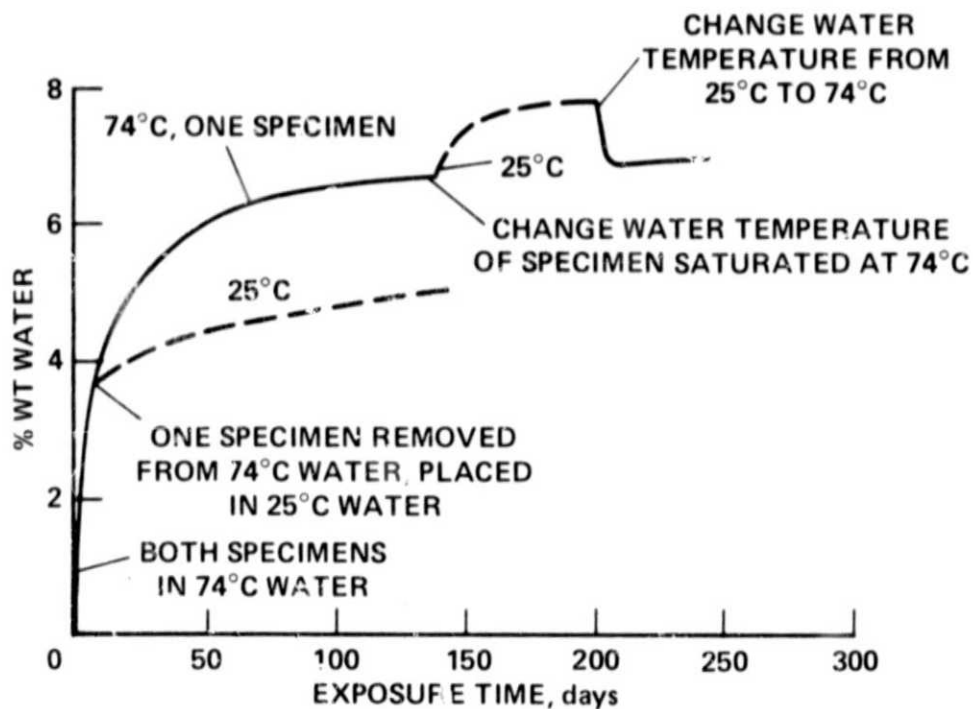


Figure 3.- Reverse-thermal-effect. Hercules 3501 resin, two specimens, fully immersed. Solid line represents water soak at 74° C, broken line represents water soak at 25° C. Both specimens initially immersed in 74° C water.

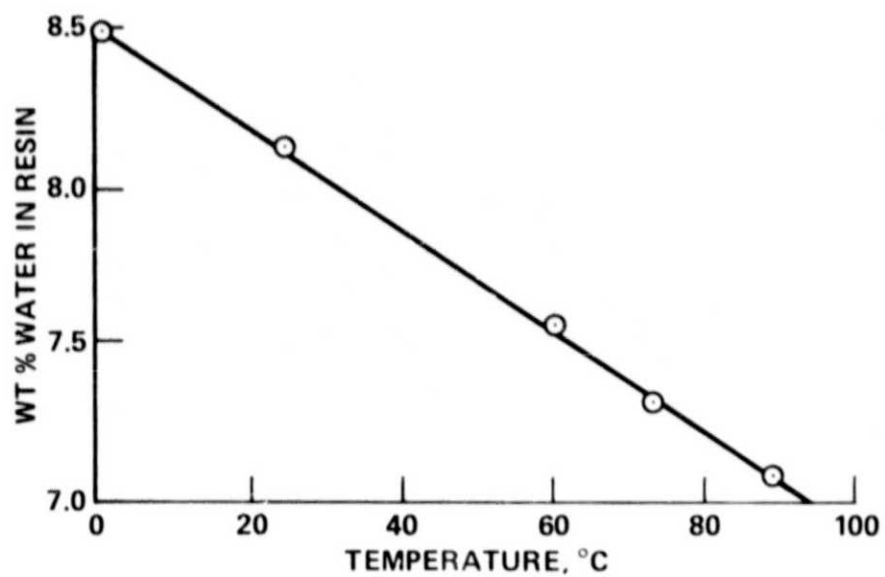


Figure 4.- Equilibrium moisture concentration as a function of temperature; one specimen Hercules 3501 resin first immersed in 74° C water to equilibrium then equilibrated in water at other temperatures shown.

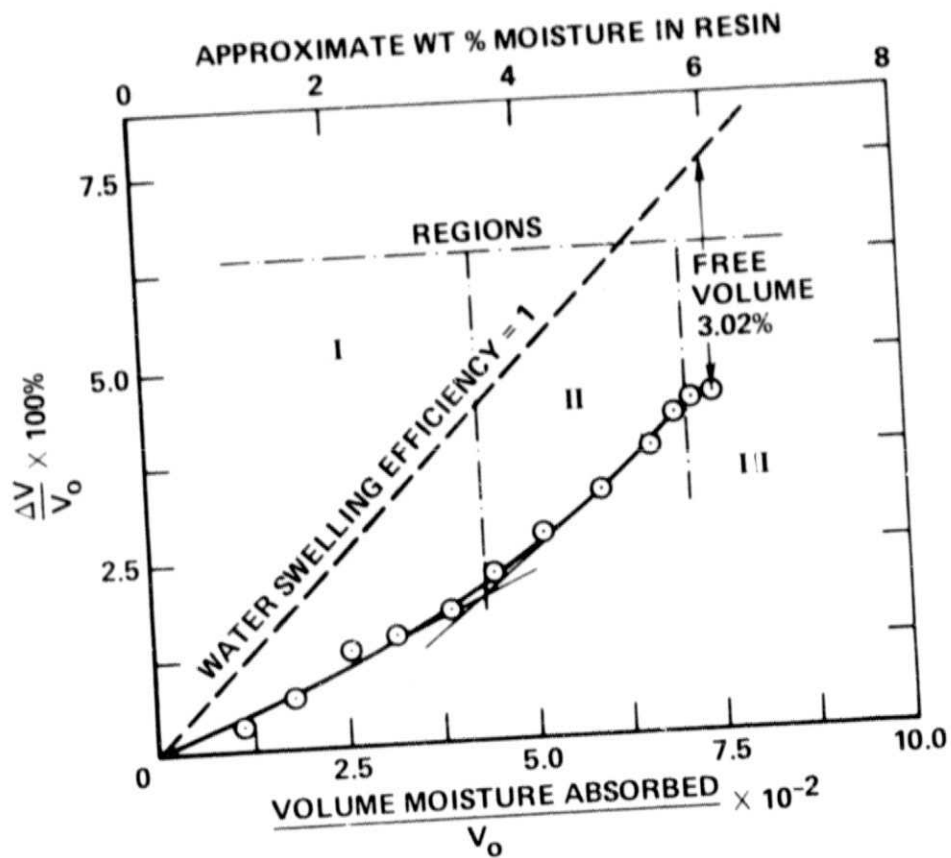


Figure 5.- Swelling efficiency of Hercules 3501 resin immersed in 40° C water.

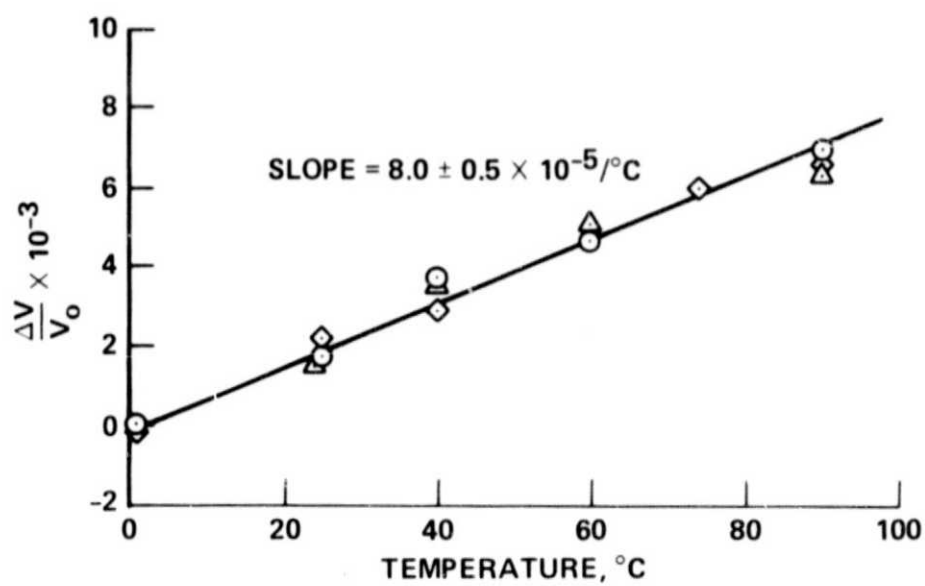


Figure 6.- Volumetric thermal expansion coefficient, Hercules 3501 resin, dry, three specimens.



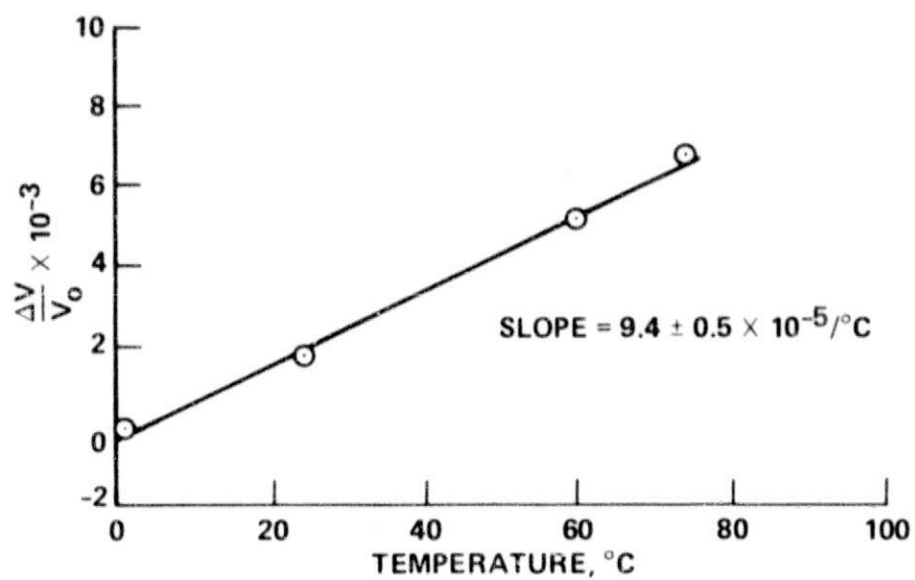


Figure 7.- Volumetric thermal expansion coefficient, Hercules 3501 resin, dry, previously saturated at 74° C, one specimen.

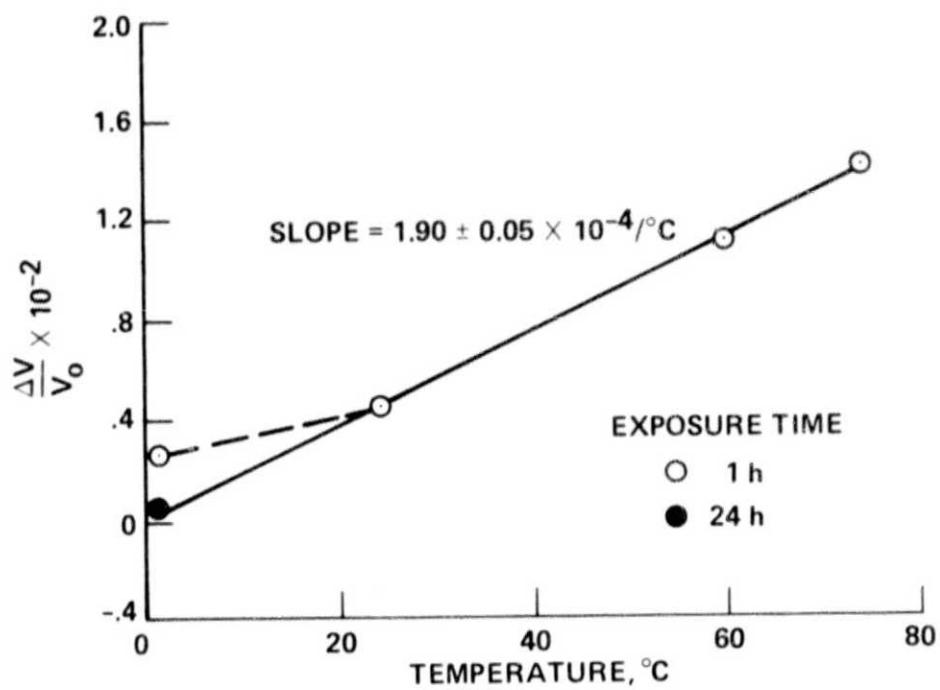


Figure 8.- Volumetric thermal expansion, Hercules 3501 resin, first immersed in 74° C water to equilibrium, then exposed to other temperatures shown, allowing no change in moisture concentration.

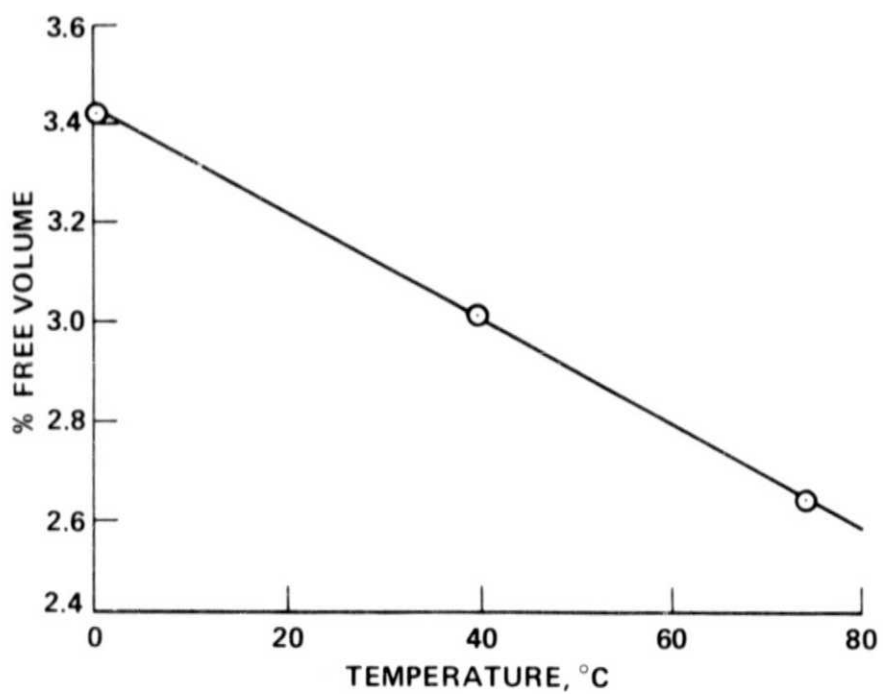


Figure 9.- Percent free volume as a function of temperature, Hercules 3501 resin. Values at 74° C and 40° C determined by swelling data during absorption. Value at 1° C determined using reverse-thermal-effect from 74° C equilibrium.